Macromolecules
COMMUNICATION TO THE EDITOR

Macromolecules **2010**, *43*, 10201–10203 **10201**
DOI: 10.1021/ma1025219

Stereoselective Polymerization of *meso*-Lactide: Syndiotactic Polylactide by Heteroselective Initiators Based on Trivalent Metals

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Received November 9, 2010

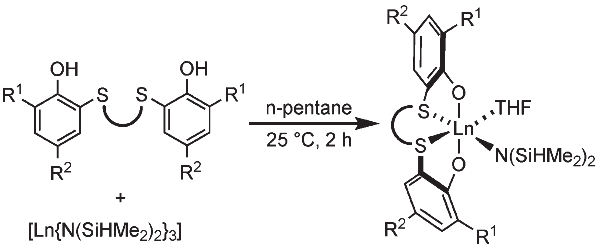
Poly(lactide) (PLA) is currently attracting considerable interest as a biodegradable thermoplastic derived from "carbon-neutral" biomass feedstocks.[1] Specifically, isotactic poly(L-lactide) has been commercialized with annual production capacity exceeding 10^5 metric tons, using L-lactide as monomer obtained by thermolysis of oligo(L-lactide).[2] During this catalytic process, significant amounts of *rac*-lactide as well as *meso*-lactide are formed as byproducts. Whereas *rac*-lactide can be polymerized to give heterotactic[3] PLA or stereocomplex PLA consisting of isotactic poly(L-lactide) and poly(D-lactide) by structurally well-defined initiators,[4] there are only few reports on syndioselective initiators for the ring-opening polymerization (ROP) of *meso*-lactide to give poly(lactide) with alternating, *R*- and *S*- stereocenters, configuration along the polymer backbone.[5] In 1999, Coates and Ovitt reported that by using an enantiopure aluminum–salen complex [Al(SalBinap)(OR)], *meso*-lactide is converted into crystalline syndiotactic poly(lactide) with T_m of 150 °C, while the yttrium complex with the same ligand was not active.[5h] Peculiarly, this work remained the only report on highly syndioselective initiators for this currently still valueless stereoisomer of L-lactide.[6]

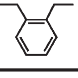
The mechanism suggested by Coates and Ovitt was based on a site control at a chiral site. It occurred to us that an initiator that polymerizes *rac*-lactide to give high heterotactic PLA should polymerize *meso*-lactide with highly syndiotacticity, provided the initiator's dynamic properties results in attack of one of the two diastereotopic sites in *meso*-lactide (Scheme 1). We report here that heteroselective initiators for *rac*-lactide based on group 3 bis(phenolate) complexes with a "temporary" chiral reaction site are in principle capable of ROP of *meso*-lactide producing highly syndiotactic PLAs.

Heteroselective rare-earth metal inititators containing a 1,*ω*-dithia-alkanediyl-bridged bis(phenolato) ligand with bulky groups at the *ortho*-substituent R^1 are readily synthesized using $[Ln\{N(SiHMe_2)_2\}_3]$[3c,d] (Figure 1). Complexes **1**–**7** polymerized *meso*-lactide rapidly at room temperature (Table 1). The molecular weights are close to calculated values (except for the extremely active initiators **2** and **4**), and the polydispersity (M_w/M_n) of the polymers are in the range 1.3–2.1 (indicative of transesterification due to the high activity of initiators **2** and **4**).

Complex **7** was previously reported to be active in the heterotactic polymerization of *rac*-lactide (>93% heterotacticity).[3c] With an initiator **7**: *meso*-lactide ratio of 1:52, full conversion is attained within 30 min in C_6D_6 with M_n of 6500 g/mol, M_w/M_n of 1.22, and syndiotacticity P_s of 0.91. An increase in the initiator: monomer ratio to 1:200 led to polymers with increased molecular weight, from 10 500 g/mol with a M_w/M_n of 1.68 (Table S1, entry 1) to 34 750 g/mol with a M_w/M_n of 2.04 (Table S1, entry 3).

The controlled behavior of the polymerization has been established using complex **7**. Variation of the [mon]/[initiator] ratio from 50 to 1000 showed linear relationship with the molecular weight experimental (Figure S2).



Bridge	-∩-	Metal	R^1	R^2	Complex
C_2	$(CH_2)_2$	Sc	^{t}Bu	Me	1
	$(CH_2)_2$	Sc	cumyl	cumyl	2
		Sc	^{t}Bu	Me	3
		Sc	cumyl	cumyl	4
		Y	cumyl	cumyl	5
C_3	$(CH_2)_3$	Sc	^{t}Bu	Me	6
C_4		Sc	^{t}Bu	Me	7

cumyl = CMe_2Ph

Figure 1. Rare-earth metal complexes **1**–**7** as ROP initiators.

Scheme 1. Proposed Mechanism for the Polymerization of *meso*-Lactide

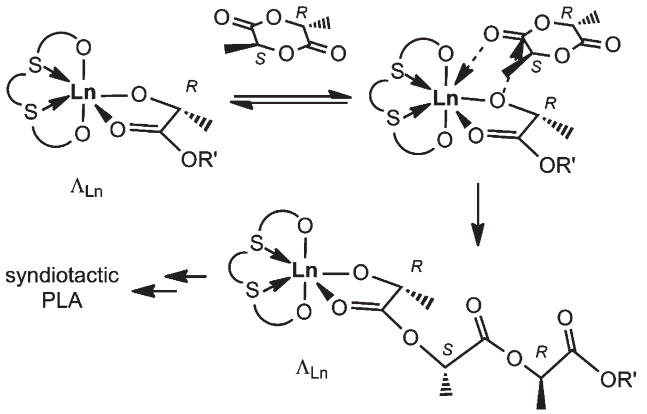


Figure 2 shows the methine region of the $^1H\{^1H\}$ NMR spectra of the PLA obtained using complex **4** and **7** containing different type of linker and *ortho*-substituents. The DSC of the sample polymerized using **4** shows a T_m of 119.1 °C, indicating partial crystallinity (Figure S22).

When initiators **1**, **3**, **6**, and **7** all with *ortho tert*-butyl substituents are compared, complex **6** with a C_3-link gave the highest syndiotacticity under the same polymerization conditions (P_s of 0.90, Table 1, entry 6). This finding is in agreement with the previously reported results for the polymerization of *rac*-lactide using **6** (95% heterotacticity).[3c] Fast conversion and high syndiotacticity were achieved with the C_2-bridged scandium derivative **2** and **4** containing *o*-cumyl substituents in the phenoxy group (P_s > 0.92). Initiators with bulkier *o*-cumyl substituents appear to give better tacticity control than those with *tert*-butyl substituents (Table 1, entries 2 and 1).

Preliminary data showed that polymerization is faster in toluene than in THF (Figure S1). The polymerization using

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Table 1. ROP of *meso*-Lactide Initiated by Complexes 1−7[a]

entry	initiator	% conv[b]	$M_{n,exp}$[c] (g/mol)	$M_{n,theo}$[d] (g/mol)	M_w/M_n[c]	P_s[e]
1	**1**	> 99	12 500	14 263	1.29	0.88
2	**2**	88	40 000	12 683	1.85	0.93
3	**3**	> 99	16 000	14 263	1.71	0.89
4	**4**	> 99	56 500	14 263	1.80	0.92
5	**5**	79	8 500	11 386	1.94	0.71
6	**6**	> 99	13 250	14 263	2.15	0.90
7	**7**	> 99	19 000	14 263	1.80	0.89

[a] Polymerization conditions: [mon]/[initiator] = 100, 25 °C, 30 min, toluene. [b] Conversion of monomer $(([mon]_0 - [mon]_t)/[mon]_0)$. [c] Measured by GPC, calibrated with PS standards in THF. [d] Calculated using $M_{n,theo} = [mon]/[initiator] \times M_{mon} \times conv$. [e] P_s is the probability for the formation of a new *s* dyad, calculated from $^1H\{^1H\}$ NMR spectra, error ±0.03 (ref 10).

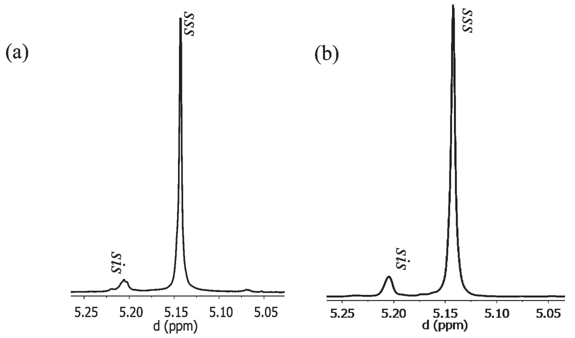

Figure 2. Homonuclear decoupled $^1H\{^1H\}$ NMR spectra of the methine region of poly(*meso*-lactide) synthesized using (a) **4** and (b) **7**.

complex **7** in THF gave polymers with molecular weights higher than those calculated, in comparison to the polymerization in toluene (Table S2). The syndiotacticity values of P_s remained at the same level (0.86). These findings indicate that the Lewis base, THF, blocks the coordination site.

Polymerization of *meso*-lactide in the melt (60, 100, and 130 °C) using scandium complex **7** (1:200) was rapid (50% monomer conversion < 10 min) and controlled (Table S3). Tacticity control ($P_s > 0.83$) was as good as that observed in solution.

In addition, scandium-based initiators were more active and more heteroselective than those based on trivalent Lewis acidic metals yttrium, lutetium, and aluminum, when used for the polymerization of *rac*-lactide.[3d] For the polymerization of *meso*-lactide using the yttrium complex **5**, a decrease in both activity and syndiotacticity was noted. With an initiator:lactide ratio of 1:100, at room temperature, the scandium complex **4** showed complete conversion within 30 min and P_s of 0.92 (Table 1, entry 4), whereas the yttrium complex **5** led to 79% conversion and P_s of only 0.71 (Table 1, entry 5).

Interestingly, Coates and Ovitt reported that the racemic aluminum−salen complex [Al(SalBinap)(OR)] polymerized *meso*-lactide to give heterotactic PLA.[5e] When enantiopure *RR*-**4** was used for ROP of *meso*-lactide under the same condition as used for racemic complex **4**, syndiotactic PLA was obtained with M_n of 57 000, M_w/M_n of 2.34, and P_s of 0.93.

The somewhat broader polydispersity of the PLAs obtained using the rare-earth metal initiators was ascribed to chain transfer reaction due to their high activity. A previously reported indium initiator,[7] which is structurally related to **1**, gave highly syndiotactic PLA (P_s of 0.93) at room temperature with M_w/M_n of 1.05 at an initiator:*meso*-lactide ratio of 1:100 and full conversion after 16 h (Table S4, entry 2).

Finally, to further test the hypothesis on the suitability of heteroselective initiators in *rac*-lactide for the syndioselective polymerization of *meso*-lactide, a C_3-symmetric zirconium alkoxide introduced by Davidson et al.[3h,8] was examined: syndiotactic PLA was obtained with M_n of 15 000, M_w/M_n of 1.17, and P_s of 0.85, corroborating that the highly heteroselective initiator offers a reaction site for syndiotactic enchainment of *meso*-lactide. (Table S4, entry 2).

In conclusion, *meso*-lactide has been efficiently polymerized by trivalent rare-earth metal initiators with a tetradentate (OSSO)-type ligand to give PLA with high syndiotacticity (P_s = 0.88−0.93). In addition to the site control mechanism operating at a stereorigid chiral ligand sphere, highly heteroselective initiators for ROP of *rac*-lactide generally appear to polymerize *meso*-lactide syndiospecifically.[9]

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support and Uhde Inventa-Fischer for a gift of *meso*-lactide.

Supporting Information Available: Synthetic procedures and characterization of **1**−**7** and polymerization data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Thomas, C. M. *Chem. Soc. Rev.* **2010**, *39*, 165–173. (b) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11–63. (c) Amgoume, A.; Thomas, C. M.; Carpentier, J.-F. *Pure Appl. Chem.* **2007**, *79*, 2013–2030. (d) Wu, J.; Yu, T.-L.; Chen, C.-T.; Lin, C.-C. *Coord. Chem. Rev.* **2006**, *250*, 602–606. (e) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147–6176. (f) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215–2224.

(2) Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv. Mater.* **2000**, *12*, 1841–1846.

(3) (a) Chamberlain, B. M.; Cheng., M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229–3228. (b) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. *Inorg. Chem.* **2004**, *43*, 6717–6725. (c) Ma, H.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7818–7821. (d) Ma, H.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2008**, *47*, 3328–3339. (e) Hodgson, L. M.; Platel, R. H.; White, A. J. P.; Williams, C. K. *Macromolecules* **2008**, *41*, 8603–8607. (f) Amgoume, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Chem.—Eur. J.* **2006**, *12*, 169–179. (g) Bonnet, F.; Cowley, A. R.; Mountford, P. *Inorg. Chem.* **2005**, *44*, 9046–9055. (h) Chmura, A. J.; Chuck, C. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Bull, S. D.; Mahon, M. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 2280–2283. (i) Du, H.; Velders, A. H.; Dijkstra, P. J.; Sun, J.; Zhong, Z.; Chen, X.; Feijen, J. *Chem.—Eur. J.* **2009**, *15*, 9836–9845.

(4) (a) Buffet, J.-C.; Okuda, J.; Arnold, P. L. *Inorg. Chem.* **2010**, *49*, 419–426. (b) Nomura, N.; Ishii, R.; Yamamoto, Y.; Kondo, T. *Chem.—Eur. J.* **2007**, *13*, 4433–4451. (c) Hormnirum, P.; Marshall, E. L.; Gibson, V. C.; Pugh, R. I.; White, A. J. P. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15343–15348. (d) Arnold, P. L.; Buffet, J.-C.; Blaudeck, R. P.; Sujecki, S.; Blake, A.; Wilson, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 6033–6036.

(5) (a) Du, H.; Velders, A. H.; Dijkstra, P. J.; Zhong, Z.; Chen, X.; Feijen, J. *Macromolecules* **2009**, *42*, 1058–1066. (b) Chisholm, M. H.; Gallucci, J. C.; Quisenberry, K. T.; Zhou, Z. *Inorg. Chem.* **2008**, *47*, 2613–2624. (c) Dove, A. P.; Li, H.; Pratt, R. C.; Lohmeijer, B. G. G.; Culkin, Da. A.; Waymouth, R. M.; Hedrick, J. L. *Chem. Commun.* **2006**, *27*, 2881–2883. (d) Amgoume, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Chem.—Eur. J.* **2005**, *12*, 169–179. (e) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316–1326. (f) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238. (g) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C.; Iyer, S. S.; Pacold, M.; Phomphrai, K. *J. Am. Chem. Soc.* **2000**, *122*, 11845–11854. (h) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072–4073.

(6) Entenmann, G.; Bendix, D. Boehringer Ingelheim, German Patent DE 3,820,299, 1988; *Chem. Abstr.* **1989**, *110*, 213592w.

(7) Peckermann, I.; Kapelski, A.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2009**, *48*, 5526–5534.

(8) (a) Chmura, A. J.; Cousins, D. M.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F. *Dalton Trans.* **2008**, 1437–1443. (b) Chmura, A. J.; Chuck, C. J.; Davidson, M. G.; Jones, M. D.; Lunn,

M. D.; Bull, S. D.; Mahon, M. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 2280–2283.

(9) A recent report by Hillmyer and Tolman et al. showed that initiators that give high heterotactic PLA may not necessarily give high syndiotacticity. Pietrangelo, A.; Knight, S. C.; Gupta, A. K.; Yao, L. J.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2010**, *132*, 11649–11657.

(10) Probability of tetrad sequences in PLA based on Bernoullian statistics: $[sss] = P_s^2 + P_sP_i/2$, $[sis] = (P_i^2 + P_iP_s)/2$, $[ssi] = [iss] = (P_sP_i)/2$ and $[isi] = P_i^2/2$.